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# THE DEPRESSION OF pH IN LAKES AND STREAMS IN CENTRAL ONTARIO DURING SNOWMELT

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# The Depression of pH in Lakes and Streams in Central Ontario During Snowmelt

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Abstract - The snow pack that accumulated in central Ontario in the winter of 1977-78 had a pH of 4.0 - 4.5. The resultant runoff in the following spring in three intensively studied watersheds was characterized by a 2-13 fold increase in $H^+$ content. Between 36 and 77% of the year's export of $H^+$ from the watersheds occurred in the month of April. Similar pH depressions were observed in almost all of 17 other streams that were less frequently sampled and in the littoral zones, surface waters and outflows of five lakes.

key words: acidification, snowmelt, hydrogen ion

Depression of pH in streams during spring runoff has been observed in Finland (Haapla et al. 1975), Sweden (Odén and Ahl 1970; Hultberg 1976) and Norway (Gjessing et al. 1976; Henriksen and Wright 1977). This effect has been attributed in all cases, to the rapid melt of an accumulated snowpack of low pH, and occurs in areas underlain by Precambrian bedrock that have overburden incapable of buffering the runoff waters. The pH's of accumulated snow in these areas are typically 4.0 - 4.5 (Scheider et al. 1978; Hultberg 1976), and this may, in fact, result in runoff that is more acidic than the snow itself. Johannessen et al. (1977) reported that in laboratory studies, the first 30% of the meltwater from a snow sample contained 70-80% of the $H^+$, $SO_4^=$ and $NO_3^-$. This meltwater normally forms a surface layer of several meters thickness which may extend over the entire surface of the lake into which it drains. For example, Hultberg (1976) observed a drop in pH of from 5.0 to 4.2 in the surface waters of Lake Timmervatten, Sweden and of from 5.0 to 3.4 in Lake Stensjon, while Dickson (1975) reported that pH declined from 4.9 to 4.5 in the mountain lake, Övre Särnamannasjön which had an accumulation of snow of pH 4.2 in its watershed. The top 2 m of Langtjern, a small lake in south-central Norway, dropped 0.4 - 0.5 pH units in all years of study (Henriksen and Wright 1977) while the upper layer in Sandtjern dropped almost 2.0 pH units (Gröterud 1972) during spring runoff. Similar findings have been reported for lakes in the LaCloche Mountain area near Sudbury, Ontario by Beamish (1974) and Yan and Stokes (1978).

Reduction in the pH of lake tributaries, surface waters and

littoral zones during the spring snowmelt period can have deleterious effects on the biota inhabiting these areas (Bell 1971; Muniz et al. 1975; Borgstrom and Hendrey 1976). In south-central Ontario the fish populations are of special interest. Those species which have acid-sensitive life stages coinciding with snowmelt may be particularly susceptible. Spawning, fry hatch and early development have previously been identified as critically sensitive stages (Almer et al. 1978). Species endemic to the region and spawning during the April-May snowmelt period include: northern pike (Esox lucius), yellow perch (Perca flavescens), walleye (Stezostedion vitreum), and introduced rainbow trout (Salmo gairdneri), (Scott and Crossman 1973). Lake trout (Salvelinus namaycush), brook trout (Salvelinus fontinalis), lake whitefish (Coregonus clupeaformis), and cisco (Coregonus artedii) spawn during the fall with egg hatch and early fry development sometimes coinciding with spring snowmelt. Many of these potentially susceptible species also comprise a significant portion of the sport fishery in south-central Ontario.

Study Area - A general description of the study area has been given by Dillon et al. (1978a). Three small streams were chosen for intensive monitoring throughout the spring runoff period. A description of the morphology, bedrock and surficial geology is given for each in Table 1, as well as average pH, alkalinity, and colour for 1977. All the streams drain small watersheds and have peak discharges of <200 L $s^{-1}$. The streams and watersheds of each lake were arbitrarily numbered for

identification. Harp Lake Inflow #4 and Paint Lake Inflow #1 are steeply sloping watersheds, each stream draining a small pond. The Dickie Lake Inflow #10 watershed is relatively flat (1-2% mean slope) with surficial deposits in the centre of the basin consisting of a sequence of peat overlaying an impermeable layer of clay up to 15 cm thick which, in turn, covers a layer of clean, well-sorted sand of variable thickness resting on bedrock. Drainage from the basin periphery passes over exposed bedrock and thin till before entering the peat layer where it obtains its high organic content and dark brown colour.

The average pH values reflect the degree of contact of precipitation with the lithographic bases in the watershed. Contact is minimal in the Dickie Lake #10 basin where the impermeable clay layer controls the drainage flow. Relatively more contact is experienced in the Harp Lake #4 and Paint Lake #1 basins with the difference in average pH between the two attributable to the shorter relative residence time of runoff within the smaller, steeper Paint Lake basin.

In addition to these three streams, 14 other streams flowing into four of the study lakes, these four lakes' outflows, and three larger rivers (Black River, Oxtongue River and Maple Creek) all in the same area were studied in the spring of 1978.

Methods - Water samples for chemical analysis were collected from Harp Lake Inflow #4, Dickie Lake Inflow #10 and Paint Lake Inflow #1 throughout most of April, 1978 using either SISCO or ISCO automatic

samplers that withdrew water from the pool formed behind the weir of each stream at intervals of 1-3 hours for about 20 days. The intakes of the samplers were positioned to prevent contamination from stream sediment or floating debris. Discharge was calculated from measurements of water velocity using either Ott C31-00 or Teledyne Gurley Pygmy model 625 current meters, taken across a surveyed section of each stream.

Grab samples were collected twice weekly from 14 other inflows and four outflows in our study area and on a daily basis from the three larger rivers noted above. Samples for chemical analysis were collected from the littoral zones of 5 lakes (Harp, Dickie, Chub, Crosson and Fawn) in the study area. All were sampled at 1 m depth at 3 locations or more using a Van Dorn bottle.

Bulk precipitation was collected by a network of samplers described by Dillon et al. (1978a). Rain samples were collected with 26.7 cm diameter funnels leading into glass bottles. Funnels were fitted with 500 μm Nitex mesh to prevent contamination by insects. Snow samples were collected with 63 cm high, 43 cm diameter polyethylene containers. Rainfall depths were measured at each collector site using 10 cm diamter polycarbonate rain gauges. Snow water equivalent depths were obtained from melted snow samples. Daily loading rates (total deposition per collection period/number of days in the period) were calculated for each collector and a mean daily load was obtained and summed to give an annual load from June 1977 - May 1978.

Chemical analyses of water samples were completed as soon as

possible after sampling, always within 24 h. A Corning Digital 109 pH meter was used to measure pH while alkalinity was determined by titration with 0.02 N $H_2SO_4$ (0.01 mol $L^{-1}$) to an endpoint of pH = 4.50. As discussed by Dillon et al. (1978a), this "total fixed-endpoint alkalinity" overestimates the true acid-neutralizing potential of water of dilute ionic composition, and thus the reported values should be considered as upper limits.

Analytical techniques are reported in detail in Ontario Ministry of the Environment (1975).

Results - Discharge, pH and hydrogen ion load for Paint Lake #1, Harp Lake #4 and Dickie Lake #10 are shown in Fig. 1a-1c for the period March 25 - May 15, 1978. The occurrence and magnitude of precipitation events are also presented. Precipitation throughout April was very light and hence had little effect on the stream discharges and calculated loadings. In all three cases, stream pH declined as discharge increased, reached a minimum at peak discharge, and increased again as pH returned to pre-runoff levels. The decline was 0.5, 1.2, and 0.3 units in Paint Lake #1, Harp Lake #4 and Dickie Lake #10 respectively, corresponding to increases in $H^+$ content from 3 to 10 μeq $L^{-1}$, 0.3 to 4 μeq $L^{-1}$ and 16 to 32 μeq $L^{-1}$.

The observation of Johannesen et al. (1977) and Johannessen and Henriksen (1977) that the initial portion of the snowmelt contains a proportionately large percentage of the ions in the snow including $H^+$ is not supported by our data. The first 33% of the runoff contributed

32, 21 and 39% of the $H^+$ load in Paint Lake #1, Harp Lake #4 and Dickie Lake #10 respectively. The hydrographs and plots of $H^+$ load are very similar in shape for all three streams.

The importance of the spring period in the annual hydrologic budget of north-temperate watersheds is well known (e.g. Likens et al. 1977; Schindler et al. 1976); the importance of this period with regard to the annual $H^+$ budget is demonstrated in Table 2. In April, 1978, the month during which almost all of the snowmelt runoff occurred, 61, 77, and 36% of the year's export of $H^+$ from the Paint Lake #1, Harp Lake #4, and Dickie Lake #10 watersheds occurred along with 45, 46 and 36% of the annual discharge. The proportionately greater input of $H^+$ in Paint Lake #1 and Harp Lake #4 is, of course, consistent with the lowered pH at this time of year.

During the period June 1977 - May 1978, we measured the input of $H^+$ from the atmosphere to be 71 meq $m^{-2}$. The output or export of $H^+$ from the three watersheds was 2.3, 0.55 and 13.5 meq $m^{-2}$ for Paint Lake #1, Harp Lake #4 and Dickie Lake #10 respectively; hence the retention of $H^+$ in the watersheds or neutralization in the streams or watersheds was 97, 99 and 81%. Therefore, all three have considerable buffering capability (or cation exchange capacity) remaining, particularly the Paint Lake and Harp Lake watersheds; however, during spring runoff and probably during major storm events the buffering reactions are not fast enough to prevent a decline in stream pH (Scheider et al. 1978).

The cations in the podzolic overburden replaced by $H^+$ include

calcium, magnesium, aluminum, and to a lesser extent manganese. Elevated aluminum and manganese levels in many lakes in the study area have been reported by Scheider et al. (1978); the possibility that calcium and magnesium concentrations are also elevated is harder to evaluate. Levels in the lakes and streams in the area are low but variable (e.g. 2-10 mg Ca $L^{-1}$), and probably dependent on the exact nature and thickness of the thin overburden in individual watersheds. Because the runoff component of the hydrologic cycle is $\simeq 0.5$ $m^3$ $m^{-2}$ $yr^{-1}$ in this part of Ontario (i.e. mean precipitation-evapotranspiration on an areal basis (Pentland 1968)), complete replacement of $H^+$ with $Ca^{++}$ would result in an increase in $Ca^{++}$ concentration in streams of 2-3 mg $Ca^{++}$ $L^{-1}$, a change that is within the natural variation found in the area.

The pH of other streams in the study area was also monitored in the spring of 1978. These included many unnamed streams draining small watersheds as well as a few large rivers. The pH in mid-March before spring runoff began is compared to that measured at peak runoff in Table 3. In all cases, an increase in $H^+$ concentration at peak runoff was observed. As expected, the small streams generally had greater changes, especially in terms of increase in $H^+$ concentration. However, even in large rivers such as the Black and Oxtongue, the pH declined. These minor pH depressions which ranged from 0.2 - 0.4 pH units were accompanied by reduction in alkalinity, from, for example, $\simeq 0.16$ to $\simeq 0.06$ meq $L^{-1}$ in the Black River and from $\simeq 0.18$ to $\simeq 0.06$ meq $L^{-1}$ in the Oxtongue River.

Because meltwater which is at or near 0°C is less dense than lakewater at 4°C, it forms an acidic surface layer which may cover the entire lake including the littoral zone to a depth of several meters, and may in part be passed through the outflow . The pH's of the outflows of Harp, Dickie, Chub and Red Chalk Lake, shown in Table 3, were all reduced in April compared to May, probably as a result of the movement of acidic water across the top of each lake. The pH's of near-surface waters (1 m) of several lakes in April 1978 are shown in Table 4. These samples included a major proportion taken in each lake's littoral zone. The decrease in comparison with measurements made during late winter under ice cover ranges from 0.7 to 1.0 pH units. The sampling technique employed does not permit evaluation of the thickness of the acidic layer, although Scheider et al. (1978) previously reported a decline to a pH of 4.2 in the top 5 m of Fawn Lake in April 1975. Acidic surface layers reported in lakes in Sweden, Norway and the Sudbury area of Ontario (Hultberg 1976; Henriksen and Wright 1977; Beamish 1974; Yan and Stokes 1978), had comparable pH depressions and varied in depth from 1 m to, in one case, the entire depth of the lake (Carlyle Lake, 12 m). The thickness of the layer will be a function of lake morphometry, meteorological factors effecting physical mixing, and relative magnitude of the runoff volume to the size of the lake (i.e. $A_d/A_o$ = watershed area/lake area).

Discussion - A large portion of south-central Ontario may potentially be affected by short-term snowmelt induced reduction of pH in streams

and littoral zones of lakes. This is a result of two factors: a) south-central Ontario has, by mid-March of each year typically 1.0 - 1.5 m of snow cover with a pH of 4.0 - 4.3 (Scheider et al. 1978), and b) as discussed by Kramer (1975), and Dillon et al. (1978a), many of the watersheds are underlain by Precambrian bedrock with only thin and scattered deposits of surficial tills of limited $H^+$ assimilation capacity. Furthermore, the spring melt may proceed quickly and run off over partially frozen soils with only partial neutralization taking place, so that the pH's of streams are reduced in even moderately well-buffered watersheds.

The effects of long-term acidification on the chemistry and biota of lakes have been well-studied (Gjessing et al. 1976; Leivestad et al. 1976; Beamish and Harvey 1972; Dickson 1975; Almer et al. 1974; Dillon et al. 1978b). The impact of short-term depressions of pH such as those occurring during snowmelt, are less well-known. Consequently, changes in biota may occur before traditional sampling programmes identify a permanent decline in pH in lakes. Although we did not attempt to evaluate the effect of exposure to acidic snowmelt on the biota, other studies have identified some likely ramifications. Borgstrom and Hendrey (1976) found that exposures of Gammarus lacustris to pH <5.5 in soft water for 45 hours killed the majority of the test animals. Survival and emergence of many aquatic insects is reduced by short exposures to low pH waters (Bell 1971). While Bell's tests were conducted at 18.5°C, it is possible that the results may be extrapolated to lower water temperatures.

Littoral zones and tributaries of lakes in central Ontario are both spawning and nursery grounds for several fish species including lake trout (Salvelinus namaycush), brook trout (Salvelinus fontinalis), whitefish (Coregonus clupeaformis), walleye (Stizostedion vitreum) and others. These populations may be affected by the low pH conditions of spring runoff. The yolk-sac stage, which appears to be the most sensitive life period for salmonids (Snekvik '69 in Hendrey and Wright 1976) often coincides with snowmelt (Scott and Crossman 1973). In a laboratory simulation of winter egg incubation at pH 8.0 and spring hatch, Trojnar (1977) found that the survival of brook trout fry decreased significantly when exposed to water at pH <5.0. In the extreme case large pH reductions during snowmelt may also result in major adult fish kills such as the one observed in the Tovdal River, Norway during March, 1975 (summarized in Lievestad et al. 1976). Unfortunately, some of the most sensitive fish species in central Ontario are highly prized sport fish such as the salmonids. The fact that we can only speculate on possible ecological effects of acidic snow-melt emphasizes the need for future studies to assess this impact.

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Table 1: Description of three watersheds; drainage area ($A_d$) in square kilometers. Chemical values are averages of 30-40 measurements excluding the spring runoff period. Colour in Hazen Units, alkalinity in meq $L^{-1}$.

| Watershed | General | Geology | | pH | Alk. | Colour |
|---|---|---|---|---|---|---|
| | Morphology | Bedrock | Surficial | | | |
| Paint Lake #1[1] ($A_d$ = 0.21 $km^2$) | Steeply sloping watershed (slope 10-20%); stream drains a small centrally located pond covering ≃5% of the total drainage area. | Biotite gneiss with minor occurrence of pegmatite dykes. | Unsorted basal till, generally <1 m thick Exposed bedrock common, particularly in stream. | 5.7 | 0.07 | 5 |
| Harp Lake #4[2] ($A_d$ = 1.24 $km^2$) | Variable slope (4-5% ave.) containing small centrally located pond covering ≃2% of the total drainage area. | Amphibolite and schist; approx. 15% is underlain by biotite gneiss. | Unsorted till (≃1 m) predominates with significant occurrence of exposed bedrock and a clean well-sorted sand. | 6.2 | 0.18 | 40 |

Table 1 - Cont'd....

| Watershed | General Morphology | Geology | | pH | Alk. | Colour |
|---|---|---|---|---|---|---|
| | | Bedrock | Surficial | | | |
| Dickie Lake #10[3] ($A_d$ = 0.66 km$^2$) | Flat lying, average slope = 1-2%. | Horneblende migmatite | Thin till and exposed bedrock predominates on the periphery while a sequence (≃1 m) of peat over clay over sand is found in the centre. | 4.7 | 0.05 | 200 |

[1]45 13' N, 78 57' W

[2]45 23' N, 79 08' W

[3]45 09' N, 79 05' W

Table 2: Monthly discharge and hydrogen ion loads and percent of annual total for Paint Lake #1, Harp Lake #4, and Dickie Lake #10 from June 1977 through May 1978.

| | Paint Lake #1 | | | | Harp Lake #4 | | | | Dickie Lake #10 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Discharge | | $H^+$ Load | | Discharge | | $H^+$ Load | | Discharge | | $H^+$ Load | |
| | $10^3m^3$ | % | Equiv. | % | $10^3m^3$ | % | Equiv. | % | $10^3m^3$ | % | Equiv. | % |
| Jun. 1977 | 0.27 | 0.2 | 0.53 | 0.1 | 6.20 | 1.0 | 2.98 | 0.4 | 0.00 | 0.0 | 0 | 0.0 |
| Jul. | 0.15 | 0.1 | 0.24 | 0.1 | 2.70 | 0.4 | 0.59 | 0.1 | 0.00 | 0.0 | 0 | 0.0 |
| Aug. | 0.00 | 0.0 | 0.00 | 0.0 | 0.00 | 0.0 | 0.00 | 0.0 | 0.00 | 0.0 | 0 | 0.0 |
| Sep. | 0.81 | 0.7 | 0.72 | 0.2 | 25.6 | 4.2 | 5.86 | 0.8 | 26.9 | 7.4 | 599 | 7.5 |
| Oct. | 10.9 | 9.3 | 16.7 | 3.4 | 61.1 | 10.0 | 26.6 | 3.6 | 76.4 | 21.1 | 2050 | 25.8 |
| Nov. | 15.5 | 13.2 | 49.1 | 10.0 | 77.1 | 12.6 | 40.9 | 5.5 | 38.2 | 10.6 | 789 | 9.9 |
| Dec. | 6.70 | 5.7 | 21.2 | 4.3 | 33.2 | 5.4 | 21.7 | 2.9 | 30.8 | 8.5 | 694 | 8.7 |
| Jan. 1978 | 3.35 | 2.9 | 7.95 | 1.6 | 21.0 | 3.4 | 9.17 | 1.2 | 11.4 | 3.2 | 139 | 1.8 |
| Feb. | 1.81 | 1.5 | 5.74 | 1.2 | 12.5 | 2.0 | 5.31 | 0.7 | 5.40 | 1.5 | 86 | 1.1 |
| Mar. | 3.85 | 3.3 | 11.4 | 2.3 | 14.8 | 2.4 | 4.53 | 0.6 | 9.80 | 2.7 | 134 | 1.7 |
| Apr. | 53.2 | 45.3 | 298 | 60.8 | 282 | 46.1 | 566 | 76.6 | 129 | 35.6 | 2870 | 36.2 |
| May | 20.9 | 17.8 | 78.9 | 16.1 | 75.7 | 12.4 | 55.4 | 7.5 | 34.1 | 9.4 | 575 | 7.5 |
| TOTAL | 117 | | 490 | | 612 | | 740 | | 360 | | 7940 | |

Table 3: pH of streams in Muskoka-Haliburton; stream pH is given prior to spring runoff (mid-March, 1978) and at maximum runoff (mid-April, 1978).

| Watershed | Stream | pH | |
|---|---|---|---|
| | | Mid-March | Mid-April |
| Harp Lake | 3 | 6.1 | 5.1 |
| | 3A | 6.0 | 5.6 |
| | 5 | 5.9 | 4.8 |
| | 6 | 6.2 | 5.3 |
| | 6A | 5.4 | 5.0 |
| | Outflow | 6.3 | 5.0 |
| Dickie Lake | 5 | 4.6 | 4.3 |
| | 6 | 4.6 | 4.4 |
| | 11 | 4.9 | 4.1 |
| | Outflow | 5.6 | 4.9 |
| Chub Lake | 1 | 5.8 | 5.1 |
| | 2 | 5.2 | 4.7 |
| | Outflow | 5.5 | 4.8 |
| Red Chalk Lake | 1 | 6.1 | 5.6 |
| | 2 | 4.5 | 4.3 |
| | 3 | 6.0 | 5.5 |
| | 4 | 6.2 | 5.5 |
| | Outflow | 6.1 | 5.9 |

Table 3 - Cont'd....

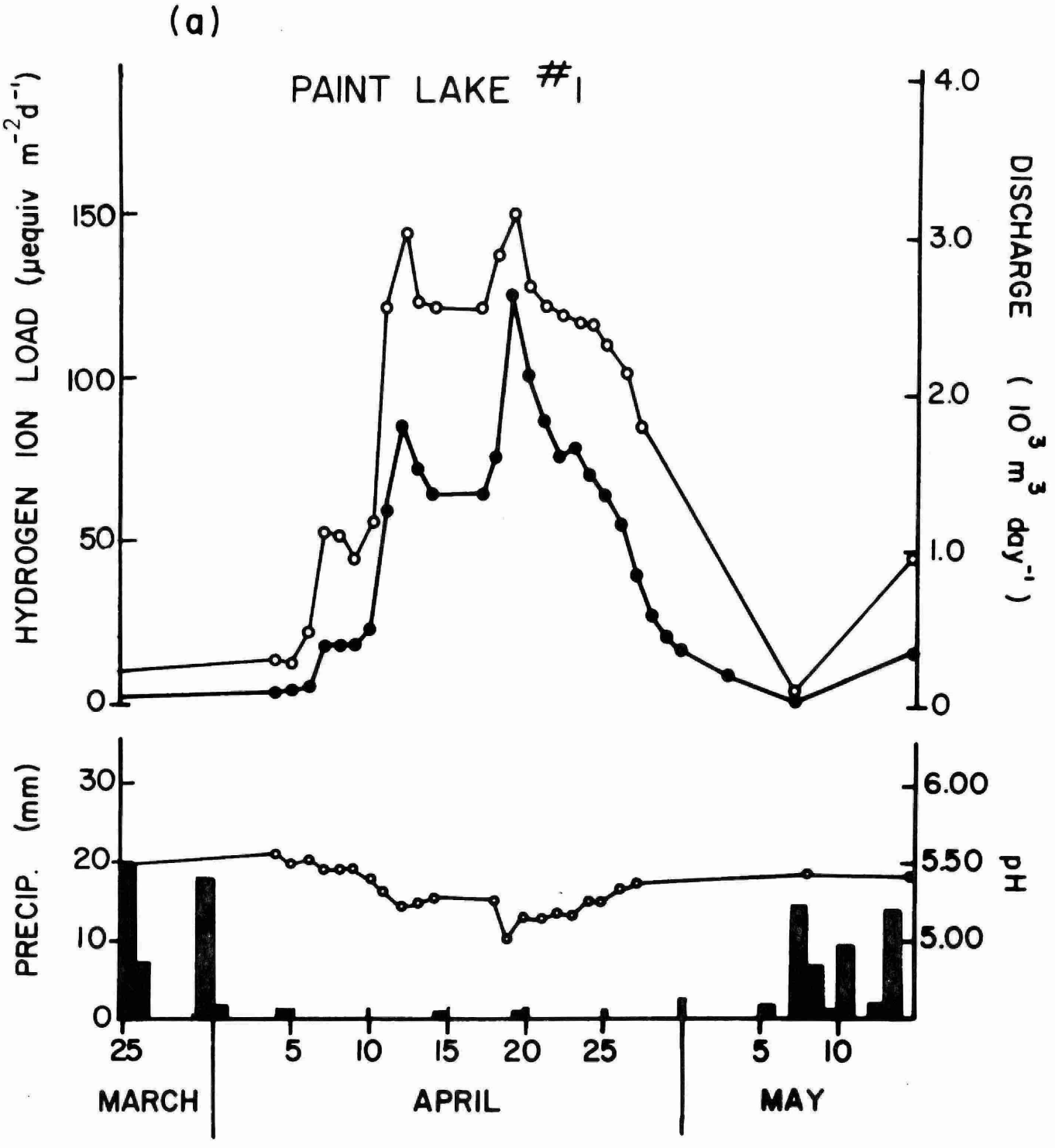
| Watershed | Stream | pH | |
|---|---|---|---|
| | | Mid-March | Mid-April |
| Maple Lake | Maple Creek | 6.2 | 5.8 |
| Lake Simcoe | Black River (at Vankoughnet) | 6.3 | 5.9 |
| Lake of Bays | Oxtongue River | 6.3 | 6.1 |

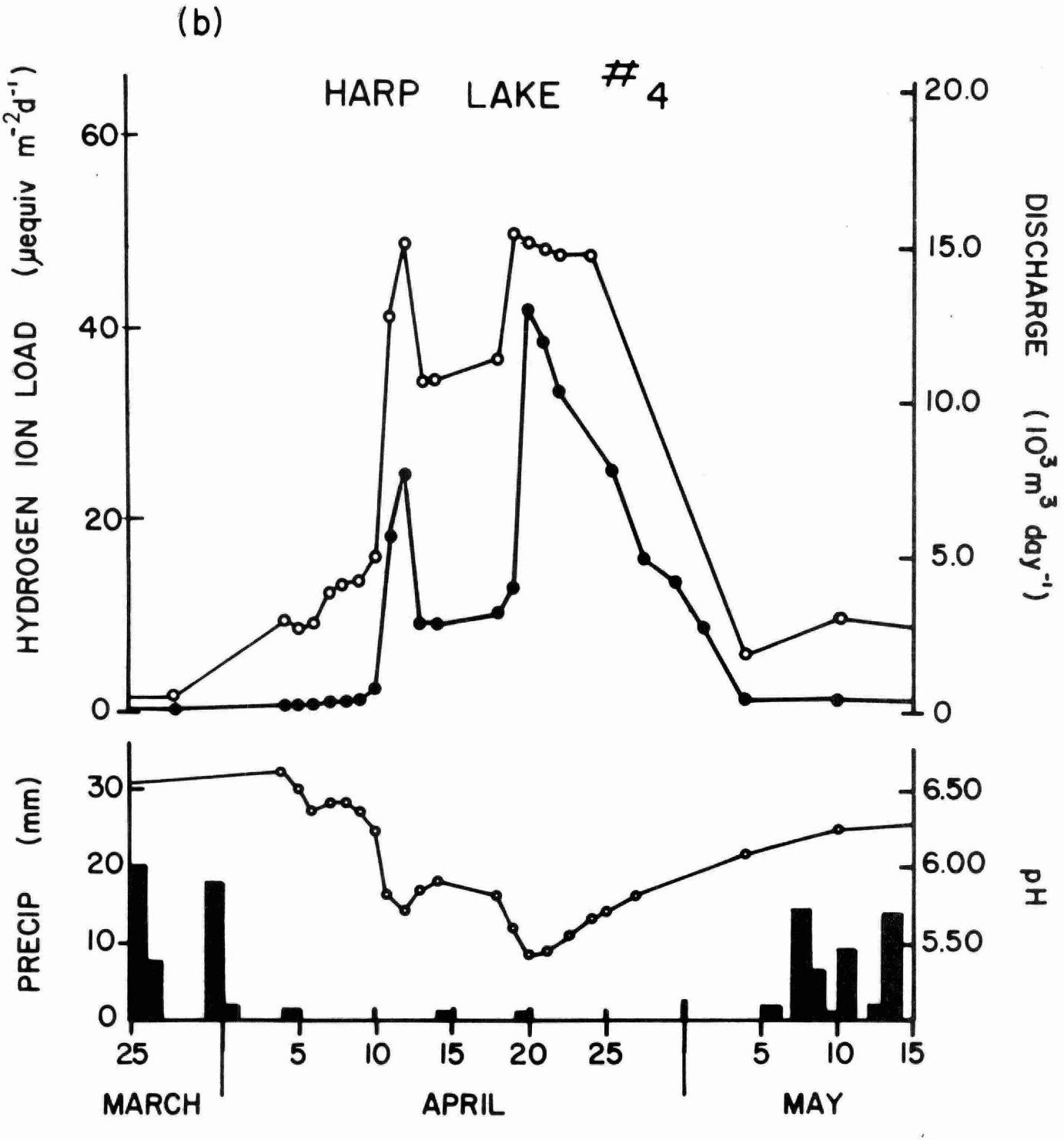
Table 4: Average pH ($-\log[H^+]_{ave.}$) at 1 m during spring runoff (April, 1978) and for whole lake in February for lakes in Muskoka-Haliburton. n is the number of sample locations at each date.

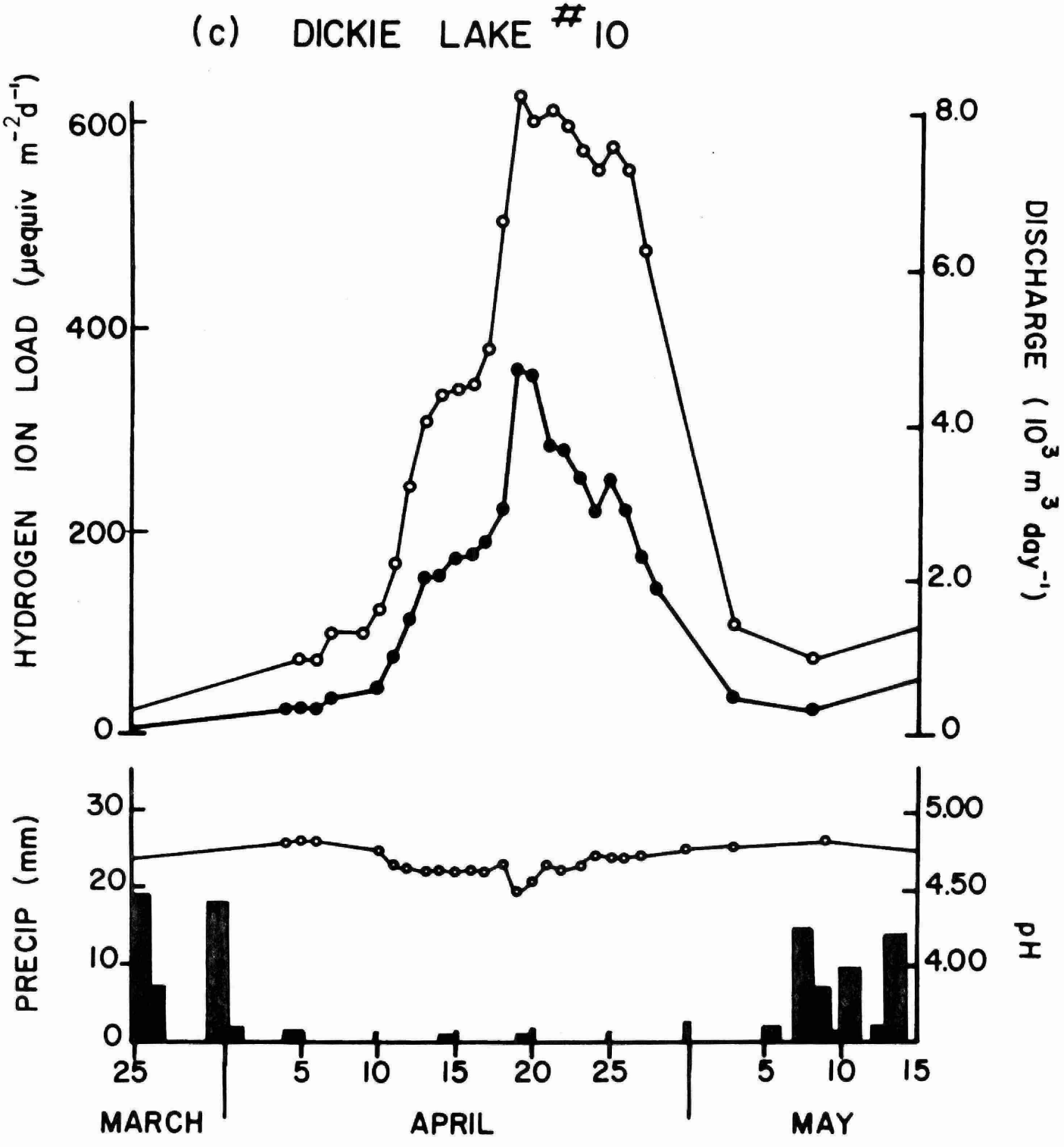
| Lake | Date Sampled | Average pH (n) | February Composite pH |
|---|---|---|---|
| Harp Lake | Apr. 12/78 | 6.2 (2) | 6.1 |
| | Apr. 19/78 | 5.4 (3) | |
| | Apr. 27/78 | 5.7 (4) | |
| Dickie Lake | Apr. 26/78 | 4.8 (6) | 5.7 |
| Chub Lake | Apr. 20/78 | 4.7 (1) | 5.7 |
| | Apr. 26/78 | 5.0 (3) | |
| Crosson Lake | Apr. 26/78 | 5.2 (5) | 6.0 |
| Fawn Lake | Apr. 10/78 | 6.3 (1) | 5.8 |
| | Apr. 26/78 | 4.7 (5) | |

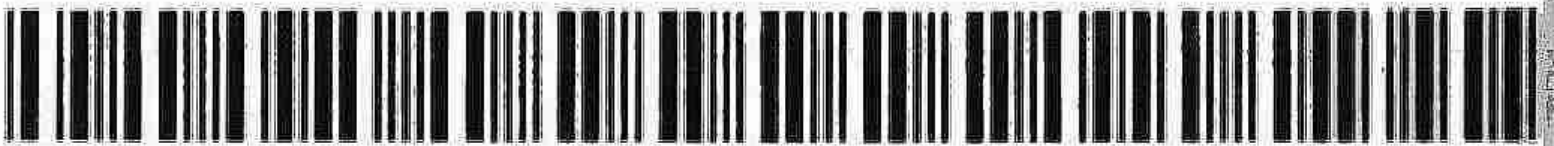
## List of Figures

Fig. 1. Discharge (open circles), hydrogen ion load per unit area of each watershed (solid circles), pH (lower graph) and depth of precipitation for each day that a precipitation event occurred for a) Paint Lake #1, b) Harp Lake #4, and c) Dickie Lake #10. The daily $H^+$ load to the respective lakes can be calculated by multiplying by the watershed area: lake area ($A_d/A_o$); where $A_d$ is the area of the subwatershed and $A_o$ that of the lake; $A_d/A_o$ is 1.85 for Harp Lake #4, 0.71 for Dickie Lake #10 and 0.14 for Paint Lake #1.


(a)
PAINT LAKE #1
HYDROGEN ION LOAD (μequiv m⁻²d⁻¹)
DISCHARGE (10³ m³ day⁻¹)
PRECIP. (mm)
pH
0
50
100
150
1.0
2.0
3.0
4.0
10
20
30
5.00
5.50
6.00
25
5
10
15
20
25
5
10
MARCH
APRIL
MAY


(b)
HARP LAKE #4
HYDROGEN ION LOAD (μequiv m⁻²d⁻¹)
DISCHARGE (10³m³ day⁻¹)
PRECIP (mm)
pH
60
40
20
0
20.0
15.0
10.0
5.0
0
30
20
10
0
6.50
6.00
5.50
25
5
10
15
20
25
5
10
15
MARCH
APRIL
MAY


(c) DICKIE LAKE # 10
HYDROGEN ION LOAD (μequiv m⁻²d⁻¹)
600
400
200
0
8.0
6.0
4.0
2.0
0
DISCHARGE (10³ m³ day⁻¹)
PRECIP (mm)
30
20
10
0
5.00
4.50
4.00
pH
25
5
10
15
20
25
5
10
15
MARCH
APRIL
MAY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